Waste Management 52 (2016) 104–111

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Acidification of In-Storage-Psychrophilic-Anaerobic-Digestion (ISPAD) process to reduce ammonia volatilization: Model development and validation

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A R T I C L E I N F O

Article history:
Received 28 November 2015
Revised 17 March 2016
Accepted 22 March 2016
Available online 6 April 2016

Keywords:
Anaerobic digestion
Ammonia
Acidification
Organic load

A B S T R A C T

In-Storage-Psychrophilic-Anaerobic-Digestion (ISPAD) is an ambient temperature treatment system for wastewaters stored for over 100 days under temperate climates, which produces a nitrogen rich digestate susceptible to ammonia (NH_3) volatilization. Present acidification techniques reducing NH_3 volatilization are not only expensive and with secondary environmental effects, but do not apply to ISPAD relying on batch-to-batch inoculation. The objectives of this study were to identify and validate sequential organic loading (OL) strategies producing imbalances in acidogen and methanogen growth, acidifying ISPAD content one week before emptying to a pH of 6, while also preserving the inoculation potential. This acidification process is challenging as wastewaters often offer a high buffering capacity and ISPAD operational practices foster low microbial populations. A model simulating the ISPAD pH regime was used to optimize 3 different sequential OLs to decrease the ISPAD pH to 6.0. All 3 strategies were compared in terms of biogas production, volatile fatty acid (VFA) concentration, microbial activity, glucose consumption, and pH decrease. Laboratory validation of the model outputs confirmed that a sequential OL of 13 kg glucose/m^3 of ISPAD content over 4 days could indeed reduce the pH to 6.0. Such OL competes feasibly with present acidification techniques. Nevertheless, more research is required to explain the 3-day lag between the model results and the experimental data.

1. Introduction

Operating between 0 and 20 °C, In-Storage-Psychrophilic-Anaerobic-Digestion (ISPAD) accommodates temperate climatic conditions such as that of Canada to treat wastewater stored for more than 100 days. The ISPAD system is sequentially batch fed without being emptied except at the end of the storage period. A minimum depth of wastewater is kept in the ISPAD when emptied to inoculate the next batch. Tested with swine manure, ISPAD released 64% of the methane potential, because of an acclimated microbial population (King et al., 2011). Operated under psychrophilic temperatures, ISPAD biogas had a low ammonia (NH_3) content as compared to mesophilic systems (King, 2011), thus conserving nitrogen to produce a digestate rich in Total Ammoniacal Nitrogen (TAN representing NH_4^+ and NH_3) (King et al., 2012). Highly susceptible to NH_3 volatilization, such digestate can contribute to the acidification of natural ecosystems and the eutrophication of surface water bodies (Hooda et al., 2000), besides losing TAN affecting its fertilizer value.

Besides TAN concentration, the two main factors controlling NH_3 volatilization are pH and temperature, simply because they determine the ratio of NH_3 to TAN. The effect of pH on the dissociation of NH_4^+ into NH_3 is described by Eq. (1). When the solution OH^- concentration exceeds that of H^+, the reaction shifts to the right and releases volatile NH_3.

$$NH_4^+ \leftrightarrow NH_3 + H^+ \tag{1}$$

The ratio of NH_3 to TAN is also affected by temperature as described by Eqs. (2) and (3) (Loehr, 1984; Olofsson, 1975):

$$\frac{NH_3}{TAN} = \frac{1}{(1 + 10^{(pK_a - \mathrm{pH})})} \tag{2}$$

$$pK_a = 0.09018 + \left(\frac{2729.92}{T}\right) \tag{3}$$

where pK_a is the negative log of the dissociation constant for NH_3 and T is temperature (K). For wastewaters with a TAN concentration of 3000 mg/L, a drop in pH from 7.0 to 6.0 resulted in a decrease in NH_3 from 0.5 mg/L to 0.015 mg/L (Bussink et al., 1994; Frost et al., 1990; Loehr, 1984; Stevens et al., 1992).

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http://dx.doi.org/10.1016/j.wasman.2016.03.043

Nomenclature

ISPAD	In-Storage-Psychrophilic Anaerobic Digestion
AD	anaerobic digestion
VFAs	volatile fatty acids
NH_3	ammonia
TAN	total ammonia nitrogen
OL	organic loading or organic load
Δt	time interval between two successive additions of substrate to the digester [Day]
A(t)	the amount of substrate to be added at time t [mg-C/L]
A_f	fixed amount of substrate to be added to the digester at time t [mg-C/L]
A_v	variable amount of substrate to be added to the digester at time t [mg-C/L]

Application of digestate during the coolest time of year and acidification of the digestate before its removal from ISPAD are two methods of reducing NH_3 volatilization. Since ISPAD digestate is land applied before the cropping season when the temperature is warming up, acidification is the preferred option to reduce NH_3 volatilization. Techniques presently used to acidify wastewaters are not only expensive but also lead to secondary environmental effects. For example, swine manure can be acidified to a pH of 5.5, using 5 kg of 18 M sulfuric acid/m^3 of manure. This technique increases the manure sulfur content, which can produce odors and, over a long-term basis, acidify the soil receiving digestate. Furthermore, this practice would destroy the ISPAD microbial communities. An alternative solution consists in using the microbial anaerobic process to acidify the ISPAD digestate one week before emptying. Acidification of anaerobic digestion (AD) systems often results from a fast change in temperature and/or organic loading rate, as volatile fatty acids (VFAs) producing acidogen can adapt and grow more quickly than VFAs consuming methanogens. For example, ISPAD acidogens produced an estimated maximum microbial growth rate (μ_{max}) of 1.10–7.9/day between 4 and 35 °C as compared to 0.19–0.60/day for methanogens (Madani-Hosseini et al., 2015a). Considering the operation of ISPAD, organic loading (OL) is the main acidification strategy as temperature is governed by ambient conditions. The acidification effect of OL was investigated for two stage AD systems, with an accompanying drop in pH of 1.5–2.6 unit after 7 days of operation (Alkaya and Demirer, 2011; Hutňan et al., 2010). Stamatelatou et al. (2003a) simulated the effects of sequentially overloading an anaerobic baffled reactor, using glucose dosages increased over time. Stamatelatou et al. (2003b) were able to accumulate sufficient VFAs to decrease the pH to 4.0. Although increasing the OL can drop the pH of AD systems, the buffering capacity of the wastewater can be a challenge. Ho (2010) showed that increasing the organic loading rate had no effect on lowering pig manure pH due to its high natural buffering capacity.

The buffering capacity of an AD reactor depends on the alkalinity of its content namely, the concentration of bicarbonate ion (HCO_3^-), ammonium (NH_4^+), and total dissolved solids. Governed by its dissolved CO_2, HCO_3^- is the main source of buffering capacity while NH_4^+ concentration is governed by the TAN content of the wastewater (Procházka et al., 2012). There is a direct positive relationship between total dissolved solids and alkalinity (Rtins and Probst, 1991). For example, municipal wastewaters offer a total solids (TS) concentration and an alkalinity of 0.0350–1.2% and 50–200 mg $CaCO_3$/L, as compared to swine manure with a 0.4–4.0% TS and a buffering capacity of 1750–7900 mg $CaCO_3$/L, respectively.

In this project, ISPAD acidification was challenging because the inoculum was obtained from a field system treating swine manure with a relatively high buffering capacity. Furthermore, the ISPAD system was almost full when sampled, implying a low microbial population, resulting from the limited OL applied at the end of the batch. At such time, OL are as low as 0.4 kg of volatile solid (VS)/m^3 of ISPAD content, whereas conventional systems receive in the range of 1.5–4.0 kg VS/m^3 of reactor.

For ISPAD inoculum from batch to batch, pH should not decrease lower than 6.0 to maintain an active methanogen population (Lahav and Morgan, 2004) while still substantially lowering NH_3 volatilization.

The main objective of this study was therefore to identify OL strategies capable of acidifying the ISPAD content within one week of emptying. This objective was achieved by: (i) using an optimization process, identifying three OL strategies capable of ISPAD acidifying to a pH of 6; (ii) using the ISPAD model, verifying the extent of ISPAD acidification using the 3 identified OL strategies; (iii) validating the model results with laboratory experiments, and; (iv) further refining acidification strategies to optimize the process cost.

Acidification of ISPAD was simulated using the model developed by Madani-Hosseini et al. (2015a) for the ISPAD system, capable of simulating pH regime, glucose and VFA concentrations and methane generation. The ISPAD model simulates all AD processes except for hydrolysis, explaining the use of glucose as OL to represent hydrolyzed sugar rich wastes. Three linearly increasing OL strategies were optimized using the ISPAD model and simulated for their acidification potential. The optimal OL strategy was determined by investigating: (i) the feeding frequency, namely the optimal time interval, Δt, between two successive additions of glucose, and; (ii) the OL or amount of glucose to be fed at each time interval. The acidification modeling was presumed to occur at 22 °C, a normal and achievable temperature for the ISPAD content in late spring and early summer, corresponding to the land spreading season. The simulation extended over 8 days to produce sufficient data to observe differences among strategies and to experimentally validate the results. Finally, the appropriate acidification strategy was selected and validated by experimentation where the inoculum was collected at the end of the storage period of an 8-year-old field ISPAD system treating swine manure.

2. Materials and methods

2.1. The ISPAD model

The ISPAD model developed by Madani-Hosseini et al. (2015a) was used to optimize the acidification strategy using a linearly increasing OL fed at a fixed time interval. The ISPAD model is based on carbon balance and was specifically designed to:

(i) simulate a sequentially fed batch reactor totally emptied at intervals of at least 100 days, except for a volume remaining to inoculate the new batch;
(ii) adjust microbial kinetics to a range of temperatures between 4 and 35 °C using a temperature function, covering psychrophilic and mesophilic conditions (Madani-Hosseini et al., 2014);